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(54) INK JET PRINTING LIQUID

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain a water-based ink jet printing liquid capable of giving highly water-resistant printed matter for any image-receiving material by adding a pigment to an ethylenically unsaturated monomer followed by emulsion polymerization in the presence of a surfactant, etc.

SOLUTION: This printing liquid is obtained by incorporating (A) 100 pts.wt. of a radical-polymerizable ethylenically unsaturated monomer such as methyl methacrylate, ethyl acrylate or α-methylstyrene with (B) 1-15 pts.wt. of a pigment such as Monoazo Yellow followed by emulsion polymerization in the presence of (C) 0.1-10 pts.wt. of a surfactant such as an alkylphenol ether-based reactive surfactant, (D) 0.1-5 pts.wt. of a polymerization initiator such as t-butyl hydroperoxide and (E) water as the essential component in such a condition as to be ≤0.5 μm in monomer droplet size. In this case, it is preferable that, in addition to the component A, 0.1-10 pts.wt., based on the total monomer, of a carboxyl-bearing monomer such as acrylic acid is used for the purpose of improving the preservability of this printing liquid.

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CLAIMS

[Claim(s)]
[Claim 1] Surfactant after adding a pigment to the ethylenic unsaturated monomer in which a radical polymerization is possible, Polymerization initiator, Recording ink for ink jets characterized by being obtained by carrying out an emulsion polymerization, using water as an indispensable component.
[Claim 2] Recording ink for ink jets according to claim 1 characterized by using a reactive surface active agent as a surfactant.
[Claim 3] The diameter of a monomer oil droplet at the time of emulsification is 0.5. Recording ink according to claim 1 characterized by being below mum.

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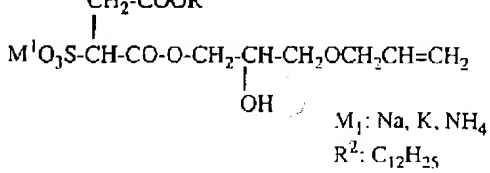
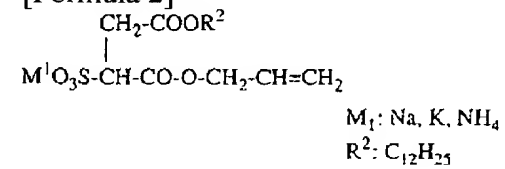
DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to recording ink excellent in the water resisting property. In more detail, though it is aquosity, it is related with the waterproof outstanding recording ink for ink jets and its waterproof manufacture approach.
[0002]
[Description of the Prior Art] As recording ink for ink jets, what dissolved water soluble dye, such as acid dye, direct dye, and basic dye, in a glycol system solvent and water is used well conventionally. However, in order to acquire the stability of the passage of time of recording ink as water soluble dye, generally the soluble high thing to water is used. Therefore, the aforementioned ink jet record object had the fault of producing a blot of the color of a record part easily, when the water resisting property was bad and generally spilt water. In order to improve such a waterproof defect, the structure of a color is changed or to adjust strong basic recording ink is tried. Moreover, aiming at waterproof improvement, using the reaction of the recording paper and recording ink well is also performed. Although these approaches are obtaining effectiveness remarkable about a certain kind of detail paper, since various detail paper is used for them in record by the ink jet method, in the recording ink which uses water soluble dye, sufficient water resisting property of a record object is not obtained in many cases.
[0003] Moreover, although there are what distributed thru/or dissolved the oil color in the high boiler as waterproof good recording ink, and a thing which dissolved the oil color in the volatile solvent, depending on the installation of the case where it may be disliked on an environment to the odor of a solvent, or discharge of a solvent, and a lot of record is performed, or equipment, needs, such as solvent recovery, may pose a problem. Furthermore, after dissolving an oil color in an organic solvent, the method of distributing water and obtaining water color ink is indicated by JP,62-2073,A. Though it was aquosity according to this approach, waterproof good recording ink was obtained, but when it was not able to say that the solubility to the organic solvent of an oil color is not necessarily enough but water was distributed, it is difficult to make color concentration high, and it was not able to obtain a high-concentration image. Moreover, since recording ink contained many organic solvents, there were also an odor of a solvent and a problem of discharge.
[0004] Therefore, in order to receive the water resisting property of a record object, development of the recording ink which distributed the pigment to the drainage system medium is performed. However, in order to acquire the distributed stability of a pigment, detailed-ization of enough pigments is needed and the technique which can do detailed pigment-content powder in easy actuation in this manufacture is needed. The big disperser of distributed energy is also needed for distribution for detailed-izing of a pigment.
[0005]
[Problem(s) to be Solved by the Invention] the ink jet from which, as for the purpose of this invention, a waterproof good record object is obtained to any television objects -- service water -- it is in offer of sex recording ink and its easy manufacture approach.

[0006]
[Means for Solving the Problem] The first invention is the surfactant after adding a pigment to the ethylenic unsaturated monomer in which a radical polymerization is possible, Polymerization initiator, It is recording ink for ink jets characterized by being obtained by carrying out an emulsion polymerization, using water as an indispensable component. The second invention is recording ink for ink jets of the first invention characterized by using a reactive surface active agent as a surface active agent. For the third invention, the diameter of a monomer oil droplet at the time of emulsification is 0.5. Recording ink of the first invention characterized by being below mum.
[0007]
[Embodiment of the Invention] A pigment applicable to this invention is the thing of insolubility to water that what is necessary is just what is distributed to the ethylenic unsaturated monomer in which a radical polymerization is possible. As pigment used, for example "Monoazo Yellow" (Pigment Yellow 1, 116), "Disazo Yellow (Pigment Yellow 81, 83)", "Iron Oxide" (Pigment Yellow42), "Disazo Orange (Pigment Orange 13)", "Naphthol Red" (PigmentRed 5) and "Quinacridone Red" (Pigment Violet 19), "Quinacridone Red" (Pigment Red 122), "Phthalocyanine Green" (Pigment Green 7), "ChromeOxide Green (Pigment Green17)", Although "Phthalocyanine Blue (Pigment Blue 15-1, 15-3)", "Iron Oxide" (Pigment Red 101), "Carbon Black" (Pigment Black 7), etc. can be illustrated It is not limited especially. These pigments are the ethylenic unsaturated monomers 100 in which a radical polymerization is possible. It is desirable to carry out 0.1 -20 weight section use to the weight section, and it is carrying out 1 -15 weight section use more preferably. When [than this] more [in producing a blur in printing as recording ink if there are few additions of a pigment than this amount], drying worsens and it becomes less desirable in a quality of printed character.
[0008] As an ethylenic unsaturated monomer which adds a pigment (Meta) It is the monomer which consists of alkyl ester of an acrylic acid. Methyl acrylate, an ethyl acrylate, Butyl acrylate, Acrylic acid 2 Ethylhexyl one, Methyl methacrylate Ethyl methacrylate Methacrylic acid 2 Ethylhexyl, Methacrylic-acid octyl, Methacrylic-acid sterile Cyclohexyl methacrylate (meta) etc. Acrylic ester Styrene, alpha - Methyl styrene, Vinyltoluene Vinyl acetate Although propionic-acid vinyl etc. can be used, it is not limited especially. Moreover, it is an acrylic acid as a monomer which has a carboxyl group in order to improve the preservation stability of recording ink in addition to the ethylenic unsaturated monomer in which the radical polymerization of said publication is possible Methacrylic acid Maleic acid Fumaric acid It is desirable to use an itaconic acid etc. together. It is desirable to carry out 0.1 -10 weight section use of the monomer which has a carboxyl group to all monomers for this purpose. 0.1 Below in the weight section, pass to a polymerization stability pan and the water resisting property of the recording ink with which the viscosity stability by the time was bad with recording ink, and was acquired above 10 weight sections worsens.
[0009] the emulsifier used by this invention -- Nonion, an anion -- although any may be used, however in order to improve the water resisting property of recording ink, it is desirable to use a reactant emulsifier. A reactant emulsifier is the partial saturation double bond in which a radical polymerization is possible to intramolecular At least 1 It is the emulsifier of anionic [which it has more than an individual], or the Nonion nature. For example, sulfo succinate system expressed with the following general formula (1) (2) (as a commercial item) for example, Kao (stock) make -- radio-and-TV mull S-120P, S-180P, and Mitsuhiro -- formation (stock) make elemi Norian JS-2 grade -- General formula (3) Alkylphenol ether system expressed (Dai-Ichi Kogyo Seiyaku (stock) Aqualon HS- as a commercial item 10, RN-20 grade) It is mentioned. General formula (1) [0010]
[Formula 1]

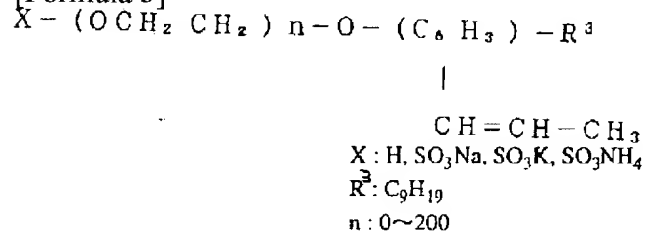


[0011] General formula (2) [0012]
[Formula 2]



M_1: Na, K, NH_4
R^2: $C_{12}H_{25}$

[0013] General formula (3) [0014]
[Formula 3]



X : H, SO_3Na, SO_3K, SO_3NH_4
R^3: C_9H_{19}
n : 0～200

[0015] An emulsion polymerization is faced and it is these 1. A kind or 2 Beyond a seed is mixed and used. These emulsifiers are the ethylenic unsaturated monomers 100 in which a radical polymerization is possible. It is desirable to carry out 0.1 -10 weight section use to weight. Above 10 weight sections, although particle diameter becomes small, it brings a result in which the water resisting property of recording ink is inferior as the bad influence in order to use a lot of emulsifiers. Radical decomposition can be carried out with heat or the reducibility matter as a polymerization initiator, the addition polymerization of an ethylenic unsaturated monomer can be made to cause in an emulsion polymerization, and it is persulfate of water-soluble or oil solubility, Peroxide, An azo system compound etc. can be used effectively. As the example, it is ammonium persulfate Potassium persulfate Sodium persulfate A hydrogen peroxide and t-butyl hydroperoxide, T-butyl peroxybenzoate, 2, 2 - Azobisisobutyronitril, 2, 2 - Azobis (2- diaminopropane) Hydro chloride, 2, 2 - Azobis (2, 4-dimethylvaleronitrile) etc. can be mentioned. As an amount of a polymerization initiator, it is the ethylenic unsaturated monomer 100 in which a radical polymerization is possible. It is 0.1-5 to the weight section. The weight section is used.
[0016] In case an emulsion polymerization is performed, it is the diameter of a monomer oil droplet of a pre emulsion 0.5 mum It is desirable to make it below and it is 0.5. mum When it is a polymerization as it is the above diameter of a monomer oil droplet, it is easy to generate an aggregate, and storage stability worsens. As an approach of making the diameter of a monomer oil droplet fine, it is a homomixer, Line mixer, High-pressure homogenizer, A supersonic wave etc. can be used and the pipe line mixer which distribution of the diameter of a monomer oil droplet can make fine narrowly further in a short time is suitable. Moreover, as a measuring method of the diameter of a monomer oil droplet, it is a diameter measuring device of a particle by the laser analysis method, An optical microscope etc. can be used.
[0017] Though it is aquosity, since the water resisting property is remarkably good, it is suitably used as recording ink for ink jets, and creation of the document in office is begun, and the recording ink manufactured by this invention is address writing of mail, Marking of corrugated paper, Numbering, It can use in fields, such as a bar code.
[0018]
[Example] Hereafter, based on an example, this invention is further explained to a detail. In addition, this invention is not limited at all by these. The section and % show weight section and weight % among an example.
(Example 1) the ethylenic unsaturated monomer presentation which is shown in Table 1 and in which a radical polymerization is possible -- a pigment "Monoazo Yellow (Pigment Yellow 1)" -- adding --

surfactant, the pipe line mixer after adding water -- the diameter of a monomer oil droplet -- 0.5 mum It is made below. Agitator, Thermometer Dropping funnel You teach the amount of reaction vessels to the reaction container equipped with the dephlegmator, and make it saturated with nitrogen gas. After carrying out the temperature up of the inside ** to 55 degrees C, the amount of reaction vessels of a polymerization initiator is added, and it is 5. Dropping was started after the part. It is a drip 1 It is dropped by time amount, a polymerization is performed among 60-65 degrees C, and it is further 1. It cools, after carrying out time amount aging, and it is pH 8-9 with ammonia. It prepared. Measurement of the diameter of an oil droplet and measurement of the particle diameter of the obtained recording ink are a diameter measuring device of a laser analysis-method particle (nano sizer by the coal tar company). It measured. Solid content 28.9%, Viscosity 100cps, particle diameter 62nm Recording ink was obtained. When this recording ink was put into the cartridge "thinkjet" by Hugh Red Packard and having been recorded in the paper of marketing for a copy, the good record object was obtained. Although water was hung down to the recording surface and the blot of ink was investigated after fully drying, there are not a blot of ink and outflow and they had sufficient water resisting property.

[0019]

[Table 1]

原料名	全量	反応缶量	滴下量
エチレン性不飽和単量体			
メタクリル酸メチル	87.5	4.4	83.1
α-メチルスチレン	54.0	2.7	51.3
アクリル酸エチル	123.1	6.2	116.9
アクリル酸	5.4	0.3	5.1
顔料			
Monoazo Yellow (Pigment Yellow 1)	27.0	1.4	25.6
反応性乳化剤			
アクアロン HS-10 *1	42.5	2.2	40.3
重合開始剤			
t-ブチルハイドロパーオキサイド *2	14.5	9.5	5.0
ロンガリット *3	36.5	36.5	0
イオン交換水	616.5	30.7	585.8
合計	1007.0		

*1 アクアロン HS-10 第一工業製薬(株)社製 有効成分20%

*2 t-ブチルハイドロパーオキサイド 有効成分5%

*3 ロンガリット 有効成分1%

[0020] (Examples 2-6) The recording ink for ink jets was prepared like the example 1 except having changed the aforementioned pigment into the following pigment. When recorded like the example 1 using these recording ink, the good record object was obtained. It is a blot of ink, although water was hung down to the recording surface and the blot of ink was investigated, There is no outflow and it had sufficient water resisting property.

The thing using example 2: "Iron Oxide" (Pigment Yellow 42).

The thing using example 3: "Naphthol Red" (Pigment Red 5).

The thing using example 4: "Chrome Oxide Green (Pigment Green 17)."

The thing using example 5: "Phthalocyanine Blue (Pigment Blue 15-1)."

The thing using example 6: "Carbon Black" (Pigment Black 7).

They are 0.8mS(s) about optimum dose, in addition electric conductivity in a sodium-hydroxide water solution to the recording ink for ink jets obtained in the examples 1-6. It adjusted above. This recording ink is a continuation injection type (sweet method). Printing stabilized from the 35-micrometer nozzle of an ink jet printer could be performed, and even if the recorded alphabetic character hung down water, it did not produce a blot or outflow of ink and showed sufficient water resisting property. Moreover, the

recording ink for ink jets obtained in the examples 1-6 could perform printing stabilized from the 40-micrometer nozzle of the ink jet printer of a method on demand, and even if the recorded alphabetic character hung down water, it did not produce a blot or outflow of ink and showed sufficient water resisting property.
(Example 1 of a comparison) The ink for ink jets was similarly adjusted except having replaced the pigment of an example 1 with water soluble dye.
(Example 2 of a comparison) The ink for ink jets was similarly adjusted except having replaced the reactant emulsifier of an example 1 with the non-reactivity emulsifier.
(Example 3 of a comparison) The ink for ink jets was similarly adjusted except having emulsified without using the pipe line mixer of an example 1.
(1) The result of having evaluated the reflection density of a record object and the water resisting property which were obtained in reflection density, the waterproof example, and the example of a comparison is shown in Table 2. In addition, it is evaluation (less than 5%, x: the fall [O: The fall of reflection density] of reflection density 5% or more) by the fall of reflection density when reflection density is measured made in Macbeth "RD-918" and a water resisting property dips a record object in 25-degree C water for 24 hours. It carried out.
(2) The result of having evaluated the storage stability of the record object obtained in the storage stability example and the example of a comparison is shown in Table 2. It judged from the viscosity change after saving for 30 days at 50 degrees C (O: for viscosity retention, x:viscosity retention is 80% the above 80% following).
[0021]
[Table 2]
【表2】

	実施例 1	実施例 2	実施例 3	実施例 4	実施例 5	実施例 6	比較例 1	比較例 2	比較例 3
反射濃度	1.4	1.4	1.4	1.4	1.4	1.4	1.0	1.4	1.0
耐水性	○	○	○	○	○	○	×	×	○
貯蔵安定性	○	○	○	○	○	○	○	○	×

[0022]
[Effect of the Invention] The recording ink for ink jet which gives a waterproof good record object by this invention though carried out through water came to be obtained. Thereby, constraint of the recorded body decreases very much and application expansion of the aquosity recording ink which producing waterproof lack under the effect of the recorded body conventionally had can be expected.

[Translation done.]